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EFFECT OF HYDROGEN PRESSURE ON THE REACTION OF NaOH-ALCOHOL-COAL.

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The reaction of coals with-alcohol-NaOH has been studied in detail[1][2] and the younger coals with less than 82%C could be dissolved nearly completely in pyridine after the reaction at 300°C for 1 hour. Even a coal of 87%C could be nearly completely dissolved by the reaction at 350°C for 1 hour. Other reaction conditions, temperature,time and the concentration of NaOH,were also examined in detail. The species of alkalis was examined,which revealed that NaOH and LiOH were most effective[3]. Reaction mechanism was pursured by the structural analysis for the pyridine extracts of which yield were more than 90%[4]. The results show that the main reaction is the hydrolysis and partly associated with hydrogenation by the hydrogen produced from the reaction between alcohol and NaOH as follows,[1][2]

$$C_2H_5OH+NaOH \longrightarrow CH_3COONa+2H_2$$

The structural analysis of pyridine extracts which represent the almost all the reaction products,that is to say the original coals themselves,revealed that the aromatic ring numbers in the structural unit (cluster unit)of the younger coals consist of 1 with 0.5 naphthenic ring and the bituminous coals have the aromatic ring number of 4 with 1 naphthenic rings. The younger coals have more of ether linkages and constitute higher molecular weight structure.

As the nascent hydrogen atoms can contribute to the hydrogenation of coal molecules,probably the atmospheric pressure affects the reaction degree and the hydrogen pressure will give more effects. This report treats the effect of hydrogen pressure on this reaction.

Experiments

Coal sample is the vitrinit of Taiheiyo coal(C:77.5%,H:6.3%, N:1.1%,S:0.2%,O_{diff}:14.5%)prepared by the float-and-sink method. The crushed coal of 1g,NaOH of 1g and 10ml of alcohol were placed in an autoclave of 38ml with the magnetic stirrer and the atmosphere was replaced with pressurized nitrogen or hydrogen.Then they were reacted at 300~430°C,for 1 hour. After reaction the gas was analyzed with GC and the product was acidified with 2N HCl. The precipitate was centrifuged,filtered,washed and dried. The extraction was carried out by shaking the product with pyridine,alcohol or benzene for 10 hours at room temperature.

At the higher reaction temperature than 400°C,the product becomes oily. Therefore benzene was added to the product and small amount of water was also added to dissolve the block of sodium acetate. The mixture of two phase solution with the unreacted powder was filtered to eliminate the unreacted part and the benzene phase was separated from aqueous phase.The benzene solution was washed well with water and dried with sodium sulfate,then benzene was recovered by distillation.The residue was extracted with benzene by shaking at room temperature as above.

IR spectra were recorded by KBr pellet with the special care to eliminate the humidity.

Results and discussion

The reaction condition,products yield and solvent extraction yield are listed in Table 1~2 and Fig 1~2. Under the nitrogen pressure the yield of ethanol extraction increases with the pressure. The main reaction of NaOH-alcohol-coal system is the hydrolysis which results the splitting of ether linkages and contributes the reduction of molecular weight[1)3)4)]. But as pointed out in the previous papers a slight hydrogenation takes place with the hydrogen produced from the reaction of alcohol with NaOH. This hydrogen is expected to act as a nascent hydrogen and under the pressure it may be confined in the solution,which contributes to the rise of reactivity.

The yield of extraction with ethanol for the products under hydrogen pressure has the higher values than those under nitrogen. The dissolution of atmospheric hydrogen into the solution may contribute to the hydrogenation.

The rise of temperature also increases the extraction yield. The yield of extraction with ethanol under hydrogen pressure always has the higher values than those under nitrogen pressure. The yield of extraction with benzene under nitrogen has the higher values than those under hydrogen at the lower temperature,but at the higher temperature the yield of extraction under hydrogen becomes higher. This can not be explained well. The possibility is that under hydrogen ether linkages split more than under nitrogen and the product contains more of OH groups,which favors the solubility into ethanol and limits the solubility into benzene.

(references)
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Table 1. Reaction conditions, product yield and solvent extraction yield at 300°C

Initial pressure, MPa	Species* of gas	Product yield %	Solvent extraction yield%	
			Pyridine	Ethanol
0.1	N	84.1	98.1	47.7
	H	87.0	95.6	83.5
2	N	89.1	93.7	68.4
	H	89.7	95.6	86.8
5	N	87.9	91.9	69.3
	H	86.4	97.0	91.0
8	N	87.9	95.9	74.5
	H	88.5	95.0	88.1

* N:nitrogen, H:hydrogen

Table 2. Reaction conditions, product yield and solvent extraction yield.

Reaction temperature °C	Species of gas	Product yield%	Solvent extraction yield%		
			Pyridine	Ethanol	Benzene
300	N	87.4	98.1	47.7	35.7
	H	89.7	95.6	86.8	18.4
350	N	89.2	97.5	51.1	42.9
	H	91.0	98.6	72.2	38.4
400	N	93.0	98.4	72.9	74.7
	H	–	–	85.5	85.0
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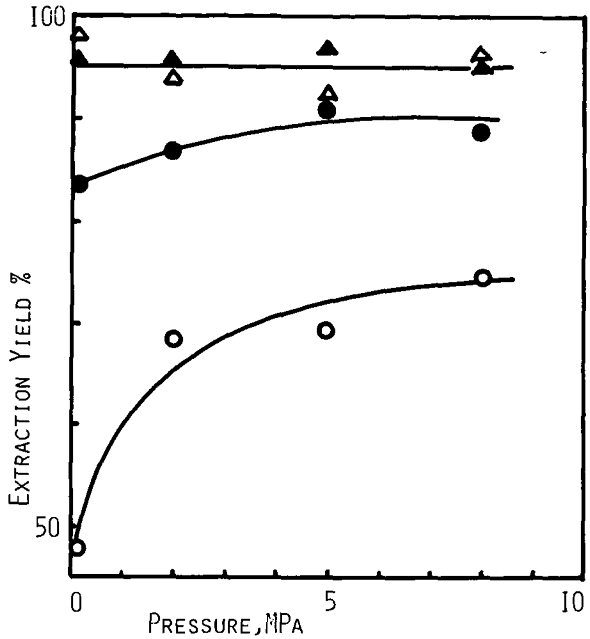
	H	–	–	–	70.8

* N:nitrogen 0.1MPa, H:hydrogen 2MPa(initial pressure)

Fig I. Pressure dependency of solvent extraction yield



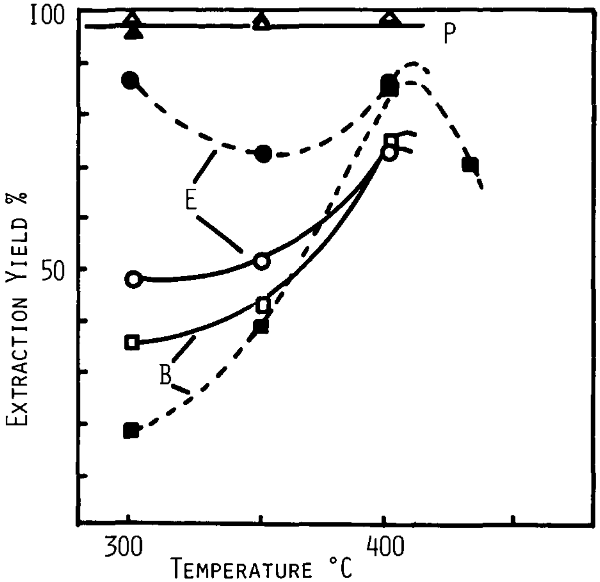
○ △ N_2

● ▲ H_2

○ ● Ethanol extraction

△ ▲ Pyridine extraction

Fig 2. Temperature dependency of solvent extraction yield



△ □ ○ N_2, 0.1MPa

▲ ■ ● H_2, 2MPa

P: Pyridine
B: Benzene
E: Ethanol